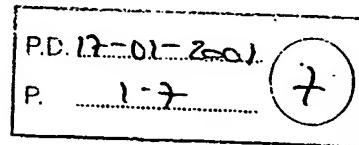


The performance of Diesel fuel manufactured by Shell's GtL technology in the latest technology vehicles

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SUMMARY

The Shell GtL (Gas-to-Liquids) technology, better known as the SMDS (Shell Middle Distillate Synthesis) process converts natural gas into novel, high quality liquid fuels via a modern, improved Fisher-Tropsch synthesis and a special hydro-conversion process. The diesel cut has very good cetane quality, low density, and virtually no sulphur and polyaromatics; such properties make it valuable as a diesel fuel with lower emissions than conventional automotive gas oil.

Concomitant with the successful restart of the Shell production plant at Bintulu Malaysia, there have been a number of improvements to the process. In particular, progress has been made in the capability of producing fuels with good cold flow characteristics without compromising cetane quality. The Shell Group has also announced its intention to build a number of World-Scale GtL plants of 70,000 bpd product capacity.

Recent studies on the performance of the SMDS diesel product are described, which complement the earlier work reported in 1999. The regulated emissions performance has been assessed in modern vehicles and engines, representing Euro-III or German DIII technologies for both light-duty vehicles and heavy-duty engines. As with earlier work on Euro-I and Euro-II systems, excellent emissions benefits are still evident with this modern technology for both the pure SMDS diesel product and also blends with a conventional diesel fuel.

1. RECENT ACTIVITIES

The Shell GtL plant at Bintulu Malaysia came back on stream in the second quarter of 2000. Since the plant shut down in late 1997, various improvements to the process and catalyst technology will increase the production capacity and allow greater flexibility in the product quality[1]. The process is outlined in Figure 1. An improved HPS (hydrocarbon synthesis) catalyst will

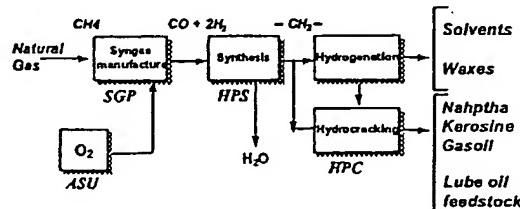


Figure 1: SMDS process at Bintulu - simplified scheme
enable the plant to increase production considerably. In addition, adjusting the severity of the

hydrocracking/isomerisation (HPC) stage allows control of the *n*- to *iso*- paraffin ratio in the final product.

At the same time when the Bintulu plant was restarted, the Shell Group announced its intention to build a number of World-Scale GtL plants of 70,000 bpd of product (cf. 12,000 bpd ex Bintulu), with the first plant due on stream around late 2005/early 2006. The SMDS diesel stream in this new GtL plant would form a larger percentage of the total products, yielding 1.4M tonne per annum. The improvements already incorporated in Bintulu together with the economies of scale from the larger plant make the economics of the GtL process competitive in an environment where crude oil prices are in the range of \$15-20/bbl.[1]

The bulk of this current paper is concerned with the latest research into the SMDS diesel product. From this viewpoint, two major areas have been investigated:-
(1) Cold flow performance of the new product and
(2) Emissions performance and benefits of SMDS diesel and SMDS diesel blends in the latest technology

vehicles and engines (complementing previous work in earlier technologies).

Analysis of the such emissions data shows the potential marketing benefits of the SMDS diesel when used either neat (100%) or in blends with conventional diesel.

2. COLD FLOW PROPERTIES

Tuning of the process conditions, in particular the hydrocracking/isomerisation step (see section 1), allows an increase in the *iso*- to *n*-alkane ratio, which results in improvement in the cold flow properties of the middle distillate fuels. Thus the process offers the ability to tailor the cold flow of the diesel to the climatic requirements of a particular market. However, with an increase in the proportion of *iso*-paraffins, one might expect a concomitant decrease of cetane number. This potential "trade-off" between cold-flow and cetane number was addressed by taking SMDS diesel samples from a pilot plant run at three conditions. Measurements of cetane number (CFR) and cold flow properties (cloud point and CFPP) were then made on these samples.

Figure 2 shows the resulting trade-off curves. In contrast to expectations, there was only a mild fall-off of cetane number with improved cold flow. Indeed, the cetane qualities are still comparable to the earlier production samples from Bintulu. The results illustrate the ability of the process to diesel fuels of good cold flow properties (-20 to -26 °C range CP/CFPP), but with no significant compromise of the cetane quality (ca. 80). This may be compared with earlier samples from Bintulu, which had CP and CFPP in the range 0 to -4°C.

In summary:-

- The cold flow is substantially improved from earlier samples, but without compromising cetane quality
- The process has sufficient flexibility meet the cold flow requirements of most markets, e.g. European winter diesel quality (-15°C).

Current experiments are now looking at the ability of cold flow additives to change the properties of SMDS diesel, potentially giving another route to tailor cold flow performance.

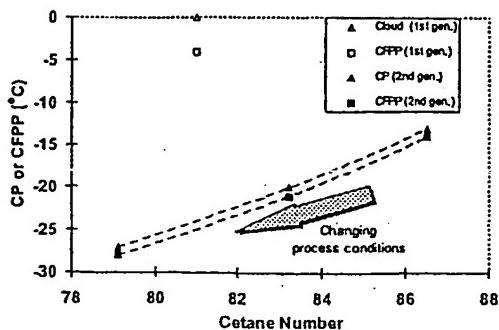


Figure 2: Cold flow-cetane trade off for SMDS diesel 2nd generation material.

3. EMISSIONS PERFORMANCE

Over the past ten years, concerns over air quality have led to environmental legislation demanding evermore tighter regulated emissions limits for on-road vehicles. Within Europe the recent legislation in this context is designated as Euro-I(1992-95), Euro-II (1996-99) and Euro-III (2000), these essentially control four regulated emissions of PM, NOx, HC and CO. To meet these stages of legislation advances in engine design have had to be made. However, there is also the potential for fuels to make a contribution.

Our earlier paper[2] looked at the potential emissions benefits of SMDS diesel over normal EU market average diesel in Euro-I and Euro-II technologies. This current work complements the earlier study by investigating whether the emissions benefits already seen are achieved in the latest technology Euro-III (2000) engines/vehicles.

3.1 Experimental Design

Whilst the low density of SMDS diesel offers a number of advantages in terms of low emissions or use as a blending stream, it can cause problems with the protocol for emissions testing. In particular, it could result in certain vehicles failing to meet the test cycle requirements when run on the 100% product. If this were the case, then SMDS would effectively be tested under less stringent conditions than the other test fuels, giving it an unfair advantage in emissions performance. For that reason SMDS was blended with a conventional diesel, in progressively increasing amounts (15%, 30%, 50%, 70%). This allows extrapolation to the 100% case. Strictly speaking of course, the full advantages of the 100% case cannot be properly assessed in an engine that has not been optimised to the product, because of the very different properties from a conventional diesel.

3.2 Test Fuel properties

The SMDS diesel was co-blended in varying proportions with a European diesel fuel meeting the CEN specification for 1996, but close to the current CEN specification for 2000. An addition to the matrix was a fuel complying with the UK Ultra Low Sulphur Diesel (ULSD) specification. **Table 1** summarises the key fuel properties.

PROPERTIES	CEN 0% SMDS,	15% SMDS blend	30% SMDS blend	50% SMDS blend	70% SMDS blend	UK ULSD
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DENSITY ^a kg/m ³ @ 15°C	850.3	837.8	826.9	811.4	798.6	834.0
DISTILLATION ^b °C						
IBP	201.0	190.0	188.0	183.5	189.5	166.0
10%	244.0	230.0	223.5	211.0	219.5	209.5
50%	290.0	288.0	286.5	282.0	280.0	281.5
90%	337.5	337.0	338.5	336.5	337.5	331.5
FBP	363.5	360.0	360.5	360.5	360.0	355.5
CETANE NUMBER	51.1	59.6	63.3	69.3	73.1	54.6
CETANE INDEX ^c	53.1	56.8	61.0	66.8	74.0	56.2
VK ^d @ 40°C CST	3.689	3.415	3.193	2.941	2.872	2.871
SULPHUR ^e %m	400	333	284	205	133	45
AROMATICS ^f , %m						
MONO	27.2	25.6	21.5	15.6	10.3	23.5
DI	4.5	4.3	3.7	2.7	1.7	4.2
TRI	0.6	0.5	0.4	0.3	0.2	0.5
TOTAL	32.3	30.4	25.6	18.6	12.2	28.2

a. IP160/ASTM D1298, b. IP123/ASTM D86, c. IP380/94,
d. IP71/ASTM D445, e. ASTM D2622, f. HPLC, IP391

Table 1: Fuel matrix properties

3.3 Vehicles, Engines and Test Cycles

A key feature of the current work was to look at the emissions performance in the very latest production technology. The chosen technology level was Euro-III or close to Euro-III. In this context the German "DIII" emissions standards represents those vehicles which can comply with the Euro-III limits, but using the old European test cycle (ECE+EUDC). Vehicle and engine details are summarised in Table 2. The heavy-duty engine complied with Euro-III. Of the light-duty vehicles, two were D-III and the other Euro-III

	Light-Duty			Heavy-Duty
Make and model	Mercedes Benz C220 CDI, 5 gear manual	Volkswagen Bora Combi, 6 gear manual	Citroen Xantia 2.0l HDI 5 gear manual	—
Emissions standard	DIII (German Standard)	DIII (German Standard)	Euro-III, homologated as Euro-II vehicle	Euro-III
Year of registration	1998	1999	1999	
Engine description	4-cylinder common rail DI, EGR, oxicat	4-cylinder unit injector DI, EGR, oxicat	4-cylinder common rail DI, EGR, oxicat	6-cylinder common rail.
Swept volume	2.151 litre	1.9 litre	1.997 litre	11 litre
Power	92 kW at 4200 r/min	85 kW at 4000 r/min	80 kW at 4000 r/min	310 kW

Table 2: Details of Test Vehicles and Engine

All 3 vehicles were tested in the MVEG cycle (the new European cycle required for Euro-III and beyond). The test and sampling was split into 3 phases but they were not regarded individually in this report. The HD engine was tested under the required Euro-III test cycle (ESC or OICA cycle).

3.4 Emissions Benefits

(a) 100% SMDS case. The emissions data from the SMDS matrix was analysed to provide estimates of the emissions benefits for use of 100% SMDS in a non-optimised engine. These benefits are illustrated in Figure 3 and then compared in Table 3 with those derived from the older technology systems (Euro-I and Euro-II).[2].

All emissions benefits seen in the earlier technology are still evident in this latest technology. Moreover, the benefits are still large and comparable in magnitude to the earlier work.[2]

Benefit (%)	Light-Duty			Heavy-Duty		
	Euro I	Euro II	Euro III	Euro I	Euro II	Euro III
PM	42	39	44	18	18	34
NOx	10	5	2	16	15	5
HC	45	63	87	13	23	<9*
CO	40	53	85	22	5	16

Table 3: Emissions benefits for 100% SMDS with respect to CEN96 LSD fuel

The major discrepancy with the earlier work is the PM and NOx for the heavy-duty engine, where PM benefits in Euro-III are significantly greater, but for NOx they are less. A larger number of engines would be required to see if this is a general effect. The result here might reflect a different tuning on the PM-NOX trade-off curve for this particular engine, thus decreasing the sensitivity of NOx to fuel effects, whilst increasing the PM sensitivity.

The heavy-duty HC measurements were so low compared to the Euro-III limits, that there were problems in distinguishing real differences between the fuels. For that reason, an upper bound to the likely HC emissions benefits was estimated.

*Estimate of upper bound of benefit.

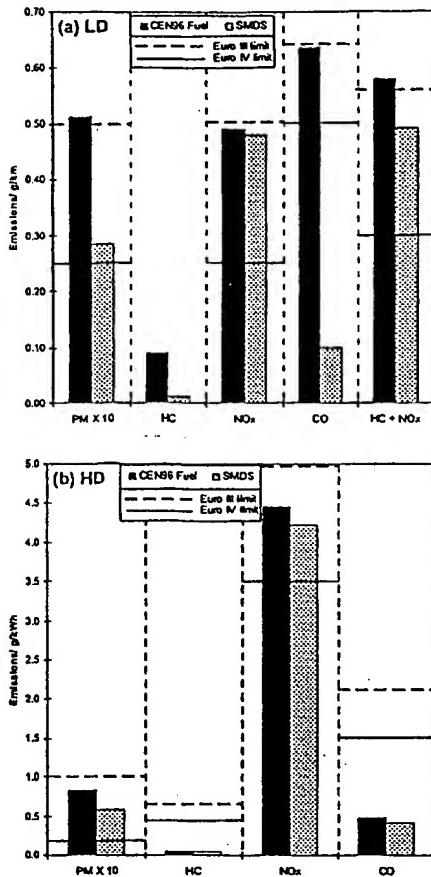


Figure 3: Regulated emissions levels (a) the mean of the light-duty D-III/Euro-III fleet and (b) the heavy-duty Euro-III engine fuelled with a CEN96 fuel and 100% SMDS (by extrapolation).

(b) SMDS Blends. As an illustration of the potential of SMDS blends with conventional diesel, the case of a 20% blend was extrapolated from the data and is given in [Table 4](#). Even at this level the resulting blend has the potential of a diesel fuel with improved environmental performance. Indeed, its performance was similar to the ULSD fuel tested in the matrix (see [Figure 4](#)), even though the conventional diesel in the blend was relatively high in density (850kg/m^3). A more detailed examination of the blending potential (see [Figure 5](#)), shows a strong non-linear effect of SMDS concentration on most of the regulated emissions. Thus, a large percentage of the emissions benefits of SMDS can be achieved for a relatively low level of SMDS diesel in the blends. Certainly, the current work has shown that blends in the 15-30% SMDS range offer a good route to achieving a low emissions fuel (even in combination with a high density fuel).

Benefit (%)	Light-Duty	Heavy-Duty
	Euro III	Euro III
PM	16	5
NOx	1	3
HC	47	<2 ^b
CO	33	3

Table 4: Emissions benefits for 20% SMDS blend with respect to the CEN fuel

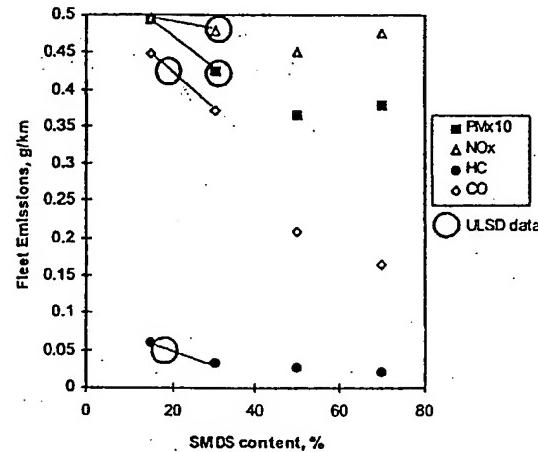


Figure 4: Light-Duty fleet regulated emissions for SMDS blends compared with UK ULSD fuel.

^bEstimate of upper bound of benefit.

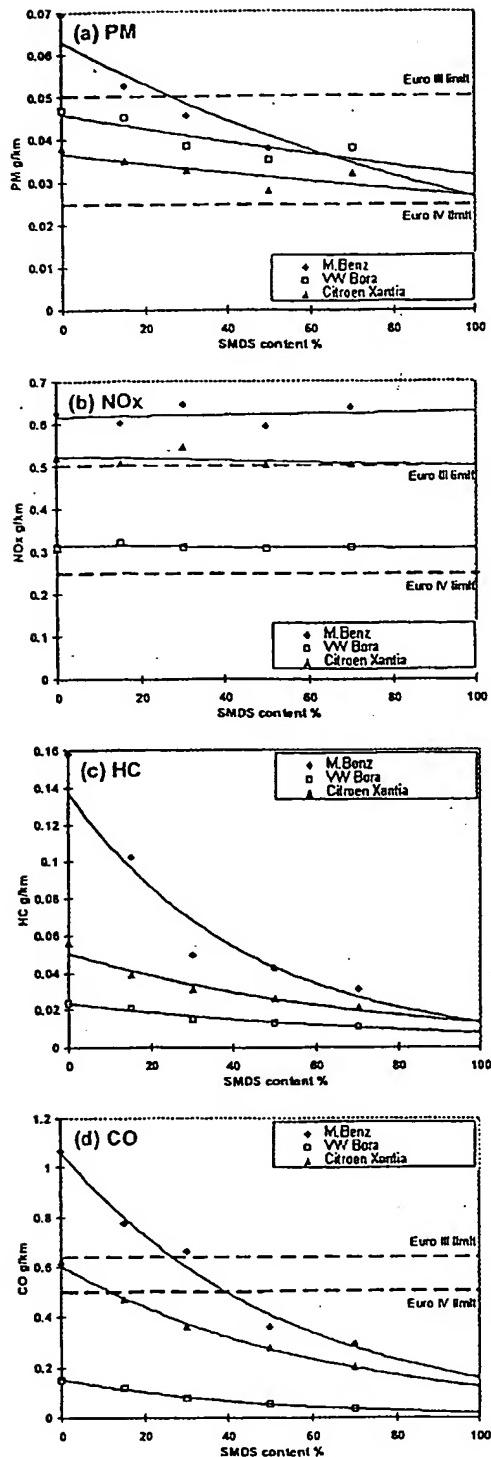


Figure 5: Regulated emissions trends extrapolated to 100% SMDS for the light-duty fleet. Where appropriate, the Euro-III and Euro-IV limits are indicated. (Where emissions lie above the Euro-III limit, this reflects the D-III vehicles in the fleet).

3.5 Potential to Reach legislation

Increasing levels of emissions benefits result from increasing levels of SMDS in the diesel blend. This trend can be viewed in the context as to whether SMDS diesel can aid an engine or one technology meet the next stage of emissions legislation, e.g "D-III" → Euro-III or Euro-III → Euro-IV.

The plots of Figure 5 show the emissions levels as a function of SMDS content and on those same plots are marked the legislative limits corresponding to Euro-III and Euro-IV. The Mercedes-Benz "D-III" vehicle is taken within the Euro-III limit for PM and CO emissions for blends of about 30% SMDS diesel. There is also a influence of SMDS on HC reduction, but the lack of a NOx effect means that the HC+NOx limits are not met.

In the case of the Citroen Xantia Euro-III vehicle, the CO is taken inside the Euro-IV limit and the PM reach within 10% of the Euro-IV limit.

	EU emissions limit met			
	Light-Duty		Heavy-Duty	
	CEN	SMDS	CEN	SMDS
PM	2	3	2	3
NOx	3	3	2	2
HC+NOx	2	3	-	-
HC	-	-	4	4
CO	2	4	4	4

Table 5(a): Potential for Euro II vehicles and engines to reach higher stages of legislation, when fuelled with SMDS diesel. (Improvements indicated in bold type)

	EU emissions limit met			
	Light-Duty		Heavy-Duty	
	CEN	SMDS	CEN	SMDS
PM	~3^c	3	3	3
NOx	3	3	3	3
HC+NOx	~3^c	3	-	-
HC	-	-	4	4
CO	3	4	4	4

Table 5(b): Potential for Euro III vehicles and engines to reach higher stages of legislation, when fuelled with SMDS diesel (Improvements indicated in bold type).

Combining these results with an analysis of our earlier paper, enables one to assess the ability of SMDS diesel in aiding Euro-I to Euro-3 technologies to meet a more severe stage of legislation. Tables 5(a) and 5(b) summarise the results.

^c~3 indicates the emissions lie on the borderline of Euro-III, due to the D-III vehicles in the fleet

Key findings were:-

- SMDS has the potential to take Euro-II light-duty fleet to Euro-3 emissions levels
- SMDS took the D-III/Euro-III fleet convincingly into the Euro-III range. CO was taken to Euro-IV

Whilst the accepted route to meet higher stages of emissions legislation is through improvements in engine design, these current findings indicate that SMDS diesel could have a role in aiding engine technology meet emissions legislation. This would be of particular interest in the context of an engine/fuel optimisation study.

4. OTHER CONSIDERATIONS

(a) In service. There are a number of other considerations which arise from the use of a fuel like SMDS diesel, which has very different properties from a conventional fuel, e.g. lubricity, elastomer compatibility and biodegradability. Such aspects have been discussed in our earlier paper.[2]

This year a biodegradability experimental study of SMDS diesel and its blends with conventional fuel has commenced, where there is an expectation that SMDS diesel will show clear benefits. In the context of unregulated PAH^d emissions, one again could envisage that SMDS diesel may have benefits over conventional diesel.

(b) Sustainability. Much interest is focused on the energy and carbon efficiency of the GtL process.

Sustainability is typically assessed against economic, social and environmental considerations. This assessment should include the entire life cycle of the process, including feedstock production, conversion and usage of products.

As a route for the production of transportation fuels and chemical feedstocks, SMDS is likely to score well on all three sustainability criteria. For example, it should offer clear lifecycle benefits for NO_x and SO₂ emissions.

On the specific issue of Greenhouse gases the comparison is more complex. Although the carbon efficiency of the SMDS process is currently lower than that of a typical leading refinery, our initial assessment is that the benefits upstream and in product usage will more than offset this.

In terms of vehicle fuel usage, SMDS diesel has a net (mass) calorific value some 2.5% greater than conventional diesel. This aspect in combination with the higher H/C ratio of the fuel (2.12 versus 1.85 for conventional diesel) could result in CO₂ per km benefits of 4-5%.

Shell is undertaking its own extensive study to confirm this total assessment.

^dPAH - polycyclic aromatic hydrocarbons

5. FUTURE WORK

This current work and our previous paper have focused on research effort within the laboratory or in engine testbeds and chassis dynamometers. There is now a strong desire to take the research and product closer to the market place. Various field trial opportunities in the EU and US are currently being explored.

6. CONCLUSIONS

The Shell Group has been active in a number of areas from the GtL process perspective:

- The Shell Group intends to build a number of World-Scale GtL plants with a 70,000 bpd product capacity, the first coming on stream in late 2005/early 2006.
- The Shell Bintulu GtL plant now successfully restarted has included improvements to the process, allowing increased production and flexibility in product properties.
- Process improvements allow the cold flow properties of the SMDS diesel to be tailored to a given market need. Cloud points and CFPP in the regime of -20°C to -26°C can be achieved with no significant compromise in the high cetane quality.
- Sustainability, CO₂ and energy efficiency issues of the GtL process are all of current interest. The expectation is that the Shell GtL system will score favourable on such issues. Verification through a detailed study is being pursued.

From the product viewpoint, the key activity has been continued testwork of regulated emissions and the associated benefits:

- Emissions testing on the latest technology vehicles and engines (D-III and Euro-III) show that considerable emissions benefits are still possible, moreover their magnitude is similar to that achieved in older technology systems.
- Blends of SMDS diesel with a conventional diesel can also achieve significant emissions benefits. Non-linear reduction of emissions with SMDS content mean that advantages are possible with low levels of SMDS, e.g. 15-30% SMDS gives results comparable to a UK ULSD fuel.
- SMDS has potential to aid an engine of one technology to meet the next stage of emissions legislation.

7. REFERENCES

- [1] M.M.G. Senden and M.W. McEwan, "The Shell Middle Distillate Synthesis (SMDS) Experience", 16th World petroleum Congress, June 2000, Calgary
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